

# Experimental determination of the volumetric properties of NaCl solutions to 253 K.

Mikhail V. Mironenko

Vernadsky Institute of Geochemistry and Analytical Chemistry  
Russian Academy of Sciences  
19 Kosygin Street  
117975 Moscow, RUSSIA  
(fax: +7 095-938-2054; E-mail: mironenko@geokhi.ru)

Ginger E. Boitnott

Steven A. Grant \*

U.S. Army Cold Regions Research & Engineering Laboratory  
72 Lyme Road  
Hanover NH 03755-1290 USA  
(fax: +1 603-646-4561;  
E-mail: ginger.e.boitnott@erdc.usace.army.mil and  
steven.a.grant@usace.army.mil)

Ronald S. Sletten

University of Washington  
Quaternary Research Center  
Box 351360  
19 Johnson Hall  
Seattle WA 98195-1360 USA  
(fax: +1 206-543-3836; E-mail: sletten@u.washington.edu)

July 23, 2001

## Abstract

The densities of 0.00858-6.0141 mol•kg<sup>-1</sup> NaCl solutions were determined between 253 and 293 K with a capillary-tube densitometer. Among the data were the first density determinations of supercooled NaCl solutions. The greatest inaccuracy of the measured densities for the entire data set was 200  $\mu\text{g}\cdot\text{cm}^{-3}$ . Our densities were close to those calculated with the equation of state for the NaCl-H<sub>2</sub>O system of Archer. Apparent molal volumes of NaCl (aq) were calculated and fitted to the Pitzer equations yielding estimated apparent molal volumes at infinite dilution and Pitzer volumetric parameters to 258 K. The values of these parameters from 273 to 298 K were in good agreement with the data of Rogers and Pitzer. From our experimental data we were able to calculate densities of very dilute to saturated sodium chloride solutions at temperatures down to 258 K.

## 1 Introduction

Electrolyte solutions below 273 K were found routinely at pressure extremes—for example, due to loading in glaciers or due to capillarity in frozen ground. The molar volumes of the solutions were needed to calculate the effect of pressure on geochemical equilibria in these systems. Unfortunately, precise volumetric data for electrolyte solutions at temperatures below 273 K were very sparse. We measured experimentally the densities of NaCl solutions to 253 K to address this gap in the published literature.

## 2 Materials and methods

The densities of NaCl solutions were determined by measuring the solution lengths in 30-cm-long 0.5-mm-inside-diameter capillaries fashioned from Pyrex glass. We fabricated an apparatus that enabled us to make precise measurements of the temperature-dependent volume changes of solutions in these capillaries. The apparatus consisted of a grooved brass cold stage embedded in an insulated box. The top of the insulated box was equipped with a viewing port for determining the lengths of the solutions in the capillaries.

---

\*Corresponding author

The temperature of the brass cold stage was controlled by heat transfer fluid circulating continuously from a Neslab constant temperature bath.

Electrolyte solutions with molalities that ranged from 0.00858 to 6.0141 mol•kg<sup>-1</sup> were prepared using A.C.S. certified crystalline NaCl and de-aerated double-deionized water. We filled a capillary by drawing up solution through an open end. This end was then sealed after assuring that no air bubbles were present. An approximately 6-cm-long column of air was left at the other end of the capillary to allow for solution volume changes. This end was then sealed also. The capillary was then placed in the groove in the cold-stage block and covered with a 6.4-mm- (1/4-inch-) thick plate glass. A schematic drawing of the apparatus was presented in Figure 1.

Solution densities were calculated by:

$$\rho_{T_f} = \frac{\rho_{T_r}}{(1 + \alpha\Delta T)^2} \times \frac{(l_{T_r} - \Delta l_{T_r})}{(1 + \alpha\Delta T)l_{T_r} - \Delta l_{T_f}} \quad (1)$$

where  $\rho_{T_f}$  and  $\rho_{T_r}$  were the solution densities (g•cm<sup>-3</sup>) at the observational temperature  $T_f$  (K) and at the reference temperature  $T_r$  (K), respectively;  $l_{T_r}$  (cm) was the length of the capillary at reference temperature;  $\Delta l_{T_r}$  and  $\Delta l_{T_f}$  (cm) were the lengths of unfilled space of the capillary at reference and observational temperatures; and  $\alpha$  was the coefficient of thermal expansion for Pyrex glass (K<sup>-1</sup>). We used the standard molal volume and Pitzer volumetric parameters from Krumgalz et al. to calculate 298.15 K reference densities of NaCl solutions at measured molalities.<sup>[7]</sup>

To test the accuracy of the device, the lengths of the unfilled spaces above de-aerated double-deionized water were measured at 263, 268, 273, 277, 278, 283, 288, 293, and 303 K. Densities were calculated using 298.15 K and 0.99705 g•cm<sup>-3</sup> as the reference density. We compared our measured densities isobaric densities calculated by the formulation of Wagner and Pruß.<sup>[9]</sup> The maximum absolute difference between measured and calculated densities was 390  $\mu$ g•cm<sup>-3</sup>. The average difference was 20  $\mu$ g•cm<sup>-3</sup>.

The lengths of the unfilled spaces above NaCl solutions were measured at 293, 288, 283, 278, 273, 268, 263, 258, and 253 K with a long working-distance microscope equipped with a linear micrometer. The accuracy of these measurements was  $\pm 0.5$   $\mu$ m. Temperature was measured at 4, 15, and 26 cm along the length of the capillary with standard platinum resistance thermometers (SPRTs). The SPRTs had NIST-traceable calibrations

with estimated accuracies of  $\pm 25$  mK. The maximum temperature gradient measured over the length of the capillary (30 mK) was observed at 253 K.

In Figure 2, we showed our experimental data points (molality versus temperature) plotted on the NaCl-H<sub>2</sub>O phase stability diagram.<sup>[4]</sup> The measured densities were presented in Table 1. The densities of representative dilute solutions as functions of temperature were presented in Figure 3. As should be expected, the dilute solutions showed density maxima near 277 K, the density maximum of the solvent. A comparison between measured and calculated densities, presented in Figure 4, illustrated that the accuracies of our measurements were better than  $\pm 200 \mu\text{g}\cdot\text{cm}^{-3}$ , though it should be noted that neither of the studies used for this comparison relied on any density measurements below 273 K.<sup>[2],[8]</sup>

### 3 Evaluation of apparent molal volumes at infinite dilution and Pitzer volumetric parameters

From these density data we estimated the apparent molal volumes at infinite dilution and Pitzer-equation volumetric parameters of the sodium chloride solutions. The solution density  $\rho$  at molality  $m$  was related to the solute apparent molal volume  ${}^\phi V$  ( $\text{cm}^3\cdot\text{mol}^{-1}$ ) through the formula

$$\rho = \frac{1000 + mM}{1000/\rho_{\text{H}_2\text{O}}^\circ + m{}^\phi V} \quad (2)$$

where  $m$  was the molality of the solution ( $\text{mol}\cdot\text{kg}^{-1}$ );  $M$  was the molecular mass of the solute ( $\text{g}\cdot\text{mol}^{-1}$ ); and  $\rho_{\text{H}_2\text{O}}^\circ$  ( $\text{g}\cdot\text{cm}^{-3}$ ) was the density of pure water. Water density was calculated with the model of Kell for temperatures at or above 273 K and with the model of Hare and Sorensen for temperatures below 273 K.<sup>[5],[6]</sup>

The Pitzer equations for apparent molal volume were used to extrapolate apparent molal volumes at any specified temperature to infinite dilution.<sup>[8],[7]</sup> The equation for a 1-1 electrolyte solution was

$${}^\phi V = \bar{V}^\circ + \frac{A_V}{b} \ln(1 + bI_m^{1/2}) + 2RT [mB^V + m^2C^V] \quad (3)$$

where  $\bar{V}^\circ$  was the apparent molal volume at infinite dilution ( $\text{cm}^3 \bullet \text{mol}^{-1}$ );  $R$ , molar gas constant ( $\text{J} \bullet \text{K} \bullet \text{mol}^{-1}$ ); and  $I_m$  ionic strength ( $\text{mol} \bullet \text{kg}^{-1}$ ). The quantity  $b$  has been assigned a value of  $1.2 \text{ kg}^{1/2} \bullet \text{mol}^{-1/2}$ .  $A_V$ , the Debye-Hückel law slope for apparent molal volume ( $\text{cm}^3 \bullet \text{kg}^{1/2} \bullet \text{mol}^{-3/2}$ ), was calculated with the Archer-Wang model for the dielectric constant of water.<sup>[1]</sup>  $B^V$  was the ionic strength-dependent virial coefficient ( $\text{kg} \bullet \text{mol}^{-1} \bullet \text{Pa}^{-1}$ ) defined by

$$B^V = \beta^{(0)V} + \beta^{(1)V} g(\alpha_1 I_m^{1/2}) \quad (4)$$

with

$$g(x) = \frac{2[1 - (1 + x) \exp(-x)]}{x^2} \quad (5)$$

and

$$\beta^{(i)V} = \left( \frac{\partial \beta^{(i)}}{\partial p} \right)_T \quad i = 0, 1 \quad (6)$$

where  $\beta^{(0)V}$  and  $\beta^{(1)V}$  were Pitzer equation volumetric ion-interaction parameters ( $\text{kg} \bullet \text{mol}^{-1} \bullet \text{Pa}^{-1}$ ) and  $p$  was pressure (Pa). The ion-interaction parameter  $C^V$  ( $\text{kg}^2 \bullet \text{mol}^{-2} \bullet \text{Pa}^{-1}$ ) was defined by

$$C^V = \left( \frac{\partial C}{\partial p} \right)_T = \frac{1}{2} \left( \frac{\partial C^\phi}{\partial p} \right)_T. \quad (7)$$

The  $\alpha_1$  parameter has been assigned value of  $2 \text{ kg}^{1/2} \bullet \text{mol}^{-1/2}$ .

The parameters  $\bar{V}^\circ$ ,  $\beta^{(0)V}$ ,  $\beta^{(1)V}$ , and  $C^V$  were estimated by minimizing the function

$$\sum_i^N [(\phi V_{i,\text{exp}} - \phi V_i) / w_i]^2 \quad (8)$$

where  $N$  was the number of apparent molal volume determinations at different molalities and

$$w_i = \frac{\partial \phi V}{\partial \rho} = \left[ \frac{1}{\rho_i^2} \left( \frac{1000}{m_i} + M \right) \right] \quad (9)$$

was the weight of the value of the apparent molal volume calculated from the measured density at molality  $m_i$ . The weight  $w_i$  reflected the error in the apparent molal volume of the solute at a given molality. This equation indicated that the expected error increased with dilution. Minimization of equation (8)

with data from dilute solutions yielded Pitzer-equation parameter estimates that were inconsistent with those obtained from more concentrated solutions. Accordingly, the parameters estimated from the nonlinear regression analysis presented in Table 2 did not include data from the dilute solutions. The dilute solutions whose densities were not included in the regression analysis are identified in Table 1. The density data from dilute solutions were presented here even though they were excluded from regression analysis in consideration for researchers who wish to compare these data with molecular dynamics calculations.

A comparison between values of apparent molal volumes at infinite dilution calculated from our data and those presented by Rogers and Pitzer was presented in Figure 5 for temperatures from 273 to 298 K.<sup>[8]</sup> It should be noted that equation (4) adopted in this study was more rigorous than the corresponding equation adopted by Rogers and Pitzer, who equated  $B^V$  with  $\beta^{(0)V}$ . The values of  $\beta^{(0)V} + \beta^{(1)V}g(\alpha_1 I_m^{1/2})$  obtained in this study were in good agreement with the values of  $\beta^{(0)V}$  tabulated by Rogers and Pitzer for 273, 283, and 293 K.

## 4 Concluding remarks

The estimated Pitzer-equation parameters can be used to calculate the densities of sodium chloride solutions over a wide range of molalities at temperatures down to 258 K as well as to estimate the pressure effect on the phase equilibria in the NaCl-H<sub>2</sub>O system. Our results were consistent with those at higher temperatures by Rogers and Pitzer<sup>[8]</sup> and the equation-of-state model by Archer and Carter.<sup>[3]</sup> These results should reassure those who extrapolate above 273 K solution-density measurements to temperatures below 273 K. Our results indicated that actual measured values were close to the values extrapolated with the volumetric Pitzer equations.

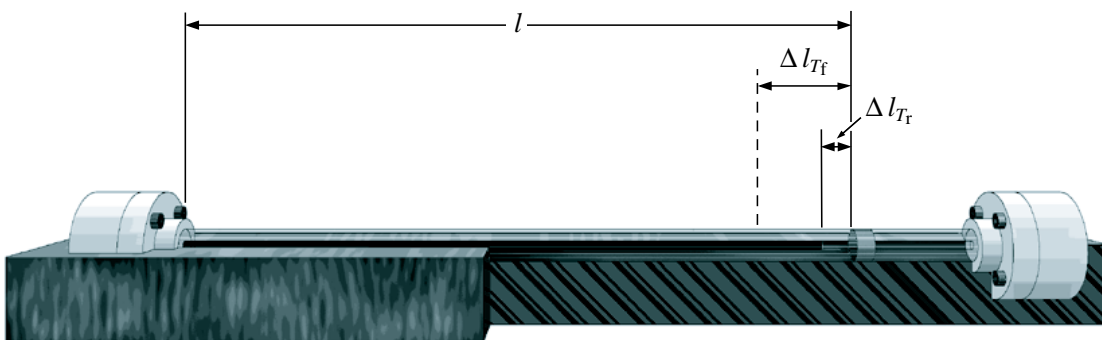
## 5 Acknowledgments

This work was supported by Radioactive Waste Management Program of the Office of International Affairs, National Research Council, U.S. Army Engineering & Development Center, work unit 61102/AT24/129/EE005, Chem-

istry of Frozen Ground, and the National Scientific Foundation project, Assessing the Risk and Dispersion Rate of Ionic Contaminants in Permafrost Terrain (OPP-99-79685).

## References

- [1] Archer, D.A.; Wang, P. *J. Phys. Chem. Ref. Data*, **1990**, *19*, 971.
- [2] Archer, D.A. *J. Phys. Chem. Ref. Data*, **1992**, *21*, 793.
- [3] Archer, D.A.; Carter, R.W. *J. Phys. Chem. B* **2000**, *104*, 8563.
- [4] Cohen-Adad, R.; Lorimer, J. *Alkali metal and ammonium chlorides in water and heavy water (binary systems), Solubility data series, Vol. 47*, Pergamon: Oxford, 1991; Chapter 2.
- [5] Hare, D.E.; Sorensen, C.M. *J. Chem. Phys.* **1987**, *87*, 4840.
- [6] Kell, G.S. *J. Chem. Eng. Data* **1967**, *12*, 66.
- [7] Krumgalz, B.S.; Pogorelsky, R.; Iosilevskii, Ya.A.; Weiser, A.; Pitzer, K.S. *J. Sol. Chem.* **1994**, *23*, 849.
- [8] Rogers, P.S.Z.; Pitzer, K.S. *J. Phys. Chem. Ref. Data* **1982**, *11*, 15.
- [9] Wagner, W.; Pruß, A. *J. Phys. Chem. Ref. Data* **200**\_ [in review] .



Boitn-001

Figure 1: Schematic drawing of the Pyrex capillary and brass cold stage with which the temperature-dependent volumes of NaCl solutions were measured.



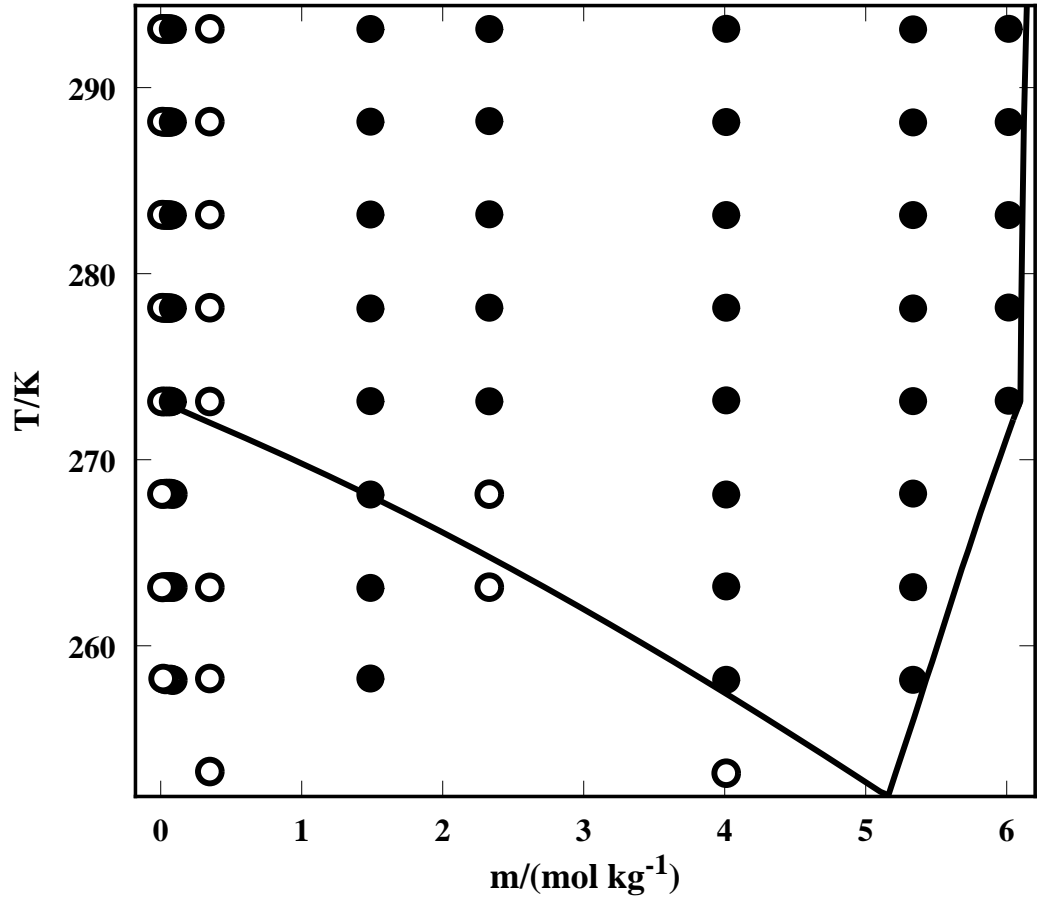


Figure 2: Equilibrium solution stability in the binary NaCl + H<sub>2</sub>O system.<sup>[4]</sup> The temperatures and molalities at which data were collected for this study are represented as circles ( $\bullet$  = observations included in the regression analysis;  $\circ$  = observations excluded from the regression analysis.)

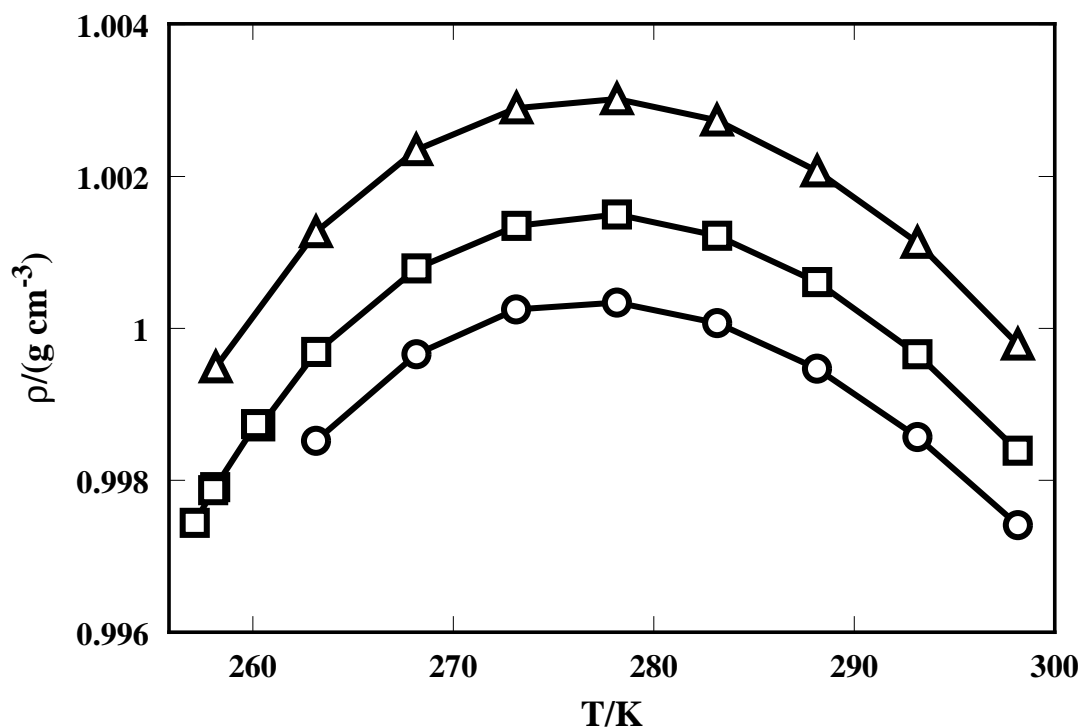


Figure 3: Experimental density data for dilute NaCl solutions at three dilute molalities presented as functions of temperature ( $\bigcirc = 0.00858 \text{ mol}\cdot\text{kg}^{-1}$ ;  $\square = 0.03430 \text{ mol}\cdot\text{kg}^{-1}$ ;  $\triangle = 0.06907 \text{ mol}\cdot\text{kg}^{-1}$ ). All of the solutions below 273 K were supercooled.

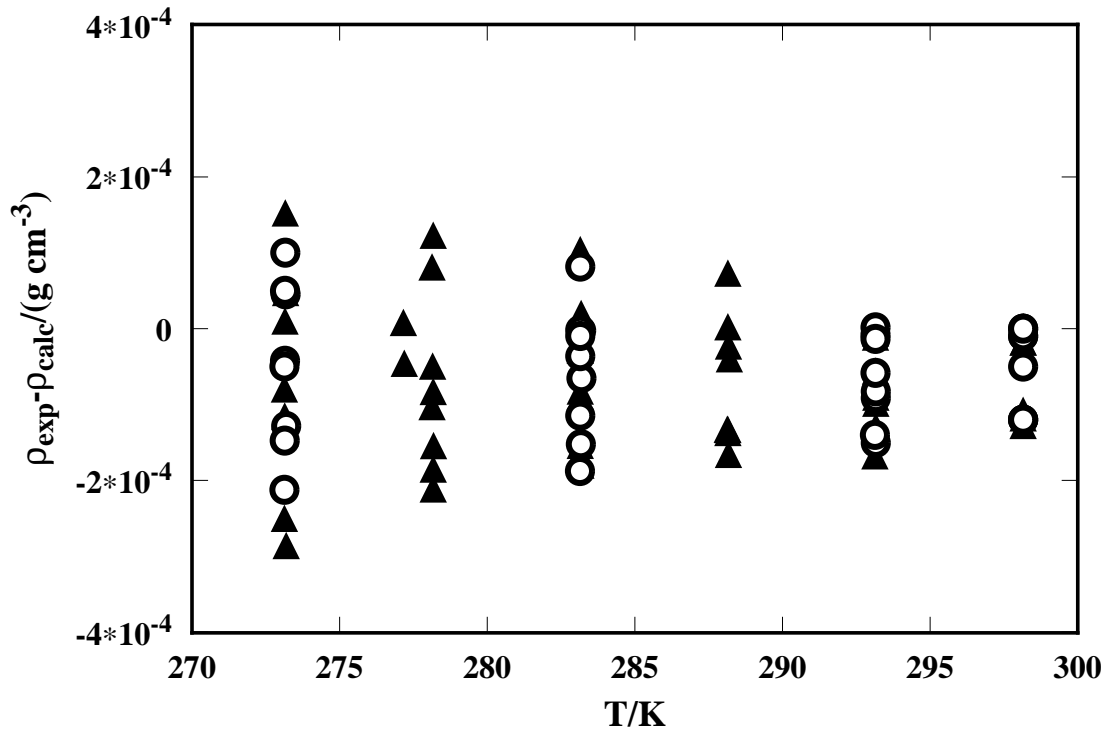


Figure 4: The difference between measured NaCl-solution densities and those calculated by the models of Archer<sup>[2]</sup> (▲) or of Rogers and Pitzer (○).<sup>[8]</sup>

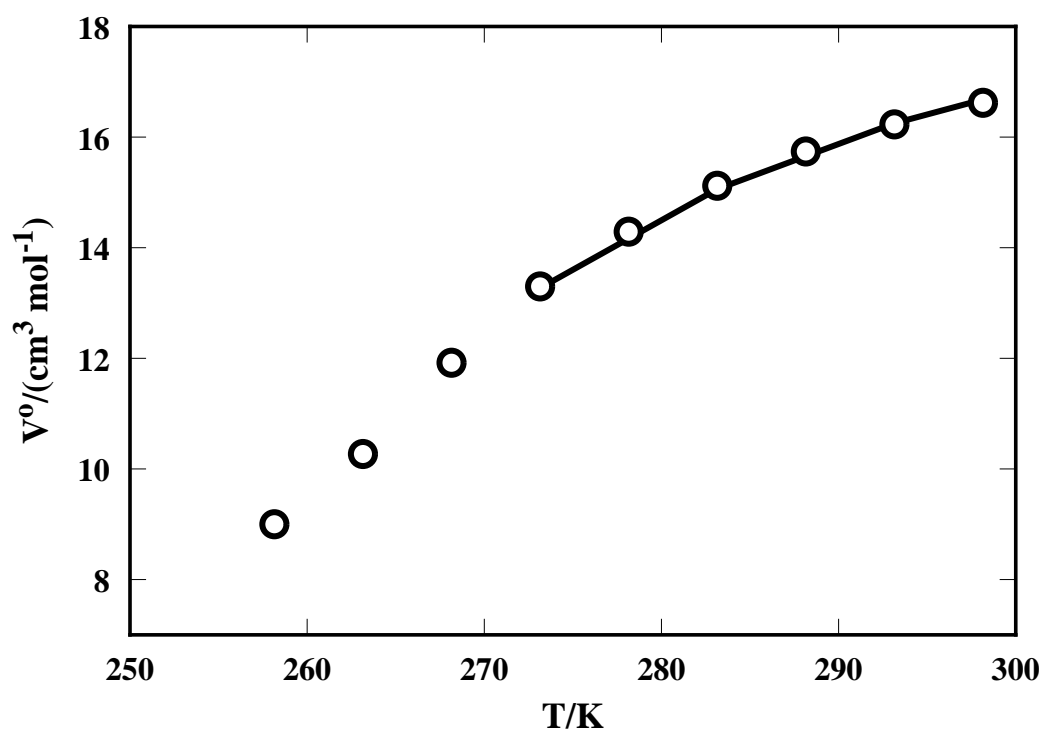


Figure 5: The apparent molal volumes at infinite dilution calculated from our experimental data (circles) and from Rogers and Pitzer (line).<sup>[8]</sup>

Table 1: Densities measured at selected molalities and temperatures.

Molality mol•kg <sup>-1</sup>	Temperature									
	K									
	293	288	283	278	273	268	263	258	253	
Density g•cm <sup>-3</sup>	Density									
	g•cm <sup>-3</sup>									
0.00858	0.99864 <sup>a</sup>	0.99954 <sup>a</sup>	1.00016 <sup>a</sup>	1.00040 <sup>a</sup>	0.99980 <sup>a</sup>	0.99923 <sup>a</sup>	0.99809 <sup>a</sup>			
0.01717	0.99895 <sup>a</sup>	0.99986 <sup>a</sup>	1.00047 <sup>a</sup>	1.00073 <sup>a</sup>	1.00052 <sup>a</sup>	0.99994 <sup>a</sup>	0.99872 <sup>a</sup>	0.99691 <sup>a</sup>		
0.01717	0.99912 <sup>a</sup>	0.99996 <sup>a</sup>	1.00061 <sup>a</sup>	1.00092 <sup>a</sup>	1.00075 <sup>a</sup>	1.00022 <sup>a</sup>	0.99911 <sup>a</sup>	0.99747 <sup>a</sup>		
0.0343	0.99976 <sup>a</sup>	1.00069 <sup>a</sup>	1.00133 <sup>a</sup>	1.00165 <sup>a</sup>	1.00149 <sup>a</sup>	1.00097 <sup>a</sup>	0.99990 <sup>a</sup>			
0.0343	0.99983 <sup>a</sup>	1.00083 <sup>a</sup>	1.00142 <sup>a</sup>	1.00166 <sup>a</sup>	1.00148 <sup>a</sup>	1.00089 <sup>a</sup>	0.99977 <sup>a</sup>			
0.0343	0.99974 <sup>a</sup>	1.00067 <sup>a</sup>	1.00131 <sup>a</sup>	1.00162 <sup>a</sup>	1.00150 <sup>a</sup>	1.00095 <sup>a</sup>	0.99992 <sup>a</sup>	0.99812 <sup>a</sup>		
0.05156	1.00034 <sup>a</sup>	1.00122 <sup>a</sup>	1.00181 <sup>a</sup>	1.00208 <sup>a</sup>	1.00197 <sup>a</sup>	1.00134 <sup>a</sup>	1.00033 <sup>a</sup>			
0.05156	1.00050 <sup>a</sup>	1.00144 <sup>a</sup>	1.00207 <sup>a</sup>	1.00242 <sup>a</sup>	1.00228 <sup>a</sup>	1.00176 <sup>a</sup>				
0.06907	1.00116 <sup>a</sup>	1.00212 <sup>a</sup>	1.00281 <sup>a</sup>	1.00311 <sup>a</sup>	1.00298 <sup>a</sup>	1.00247 <sup>a</sup>	1.00140 <sup>a</sup>			
0.06907	1.00140 <sup>a</sup>	1.00231 <sup>a</sup>	1.00298 <sup>a</sup>	1.00326 <sup>a</sup>	1.00313 <sup>a</sup>	1.00256 <sup>a</sup>	1.00148 <sup>a</sup>	0.99977 <sup>a</sup>		
0.0859	1.00178	1.00274	1.00337	1.00369	1.00362	1.00315 <sup>a</sup>	1.00213 <sup>a</sup>	1.00050 <sup>a</sup>		
0.3484	1.01264 <sup>a</sup>	1.01370 <sup>a</sup>	1.01457 <sup>a</sup>	1.01515 <sup>a</sup>	1.01536 <sup>a</sup>	1.01520 <sup>a</sup>	1.01445 <sup>a</sup>	1.01334 <sup>a</sup>	1.01156 <sup>a</sup>	
1.4871	1.05588	1.05747	1.05896	1.06030	1.06130	1.06221	1.06286	1.06320		
1.4871	1.05588	1.05757	1.05904	1.06034	1.06144	1.06233	1.06295	1.06333		
2.3304	1.08555	1.08746	1.08923	1.09087	1.09238	1.09374 <sup>a</sup>	1.09501 <sup>a</sup>			
4.0106	1.13962	1.14192	1.14416	1.14631	1.14833	1.15037	1.15224	1.15510	1.15695 <sup>a</sup>	
5.3359	1.17833	1.18089	1.18341	1.18584	1.18819	1.19048	1.19281	1.19497		
6.0141	1.19711	1.19969	1.20232	1.20476	1.20746					

<sup>a</sup> Data excluded from the estimation of Pitzer-equation parameters presented in Table 2 and the apparent molal volumes at infinite dilution presented in Figure 5.

Table 2: Apparent molal volumes of NaCl (aq) at infinite dilution and Pitzer volumetric parameters estimated in this study.

$T$	$\bar{V}^0$	$\beta^{(0)V}$	$\beta^{(1)V}$	$C^V$	$N$	$\sigma_p$
K	$\text{cm}^3 \bullet \text{mol}^{-1}$	$\text{kg} \bullet \text{mol}^{-1} \bullet \text{bar}^{-1}$	$\text{kg} \bullet \text{mol}^{-1} \bullet \text{bar}^{-1}$	$\text{kg}^2 \bullet \text{mol}^{-2} \bullet \text{bar}^{-1}$		$\mu\text{g} \bullet \text{cm}^{-3}$
298 <sup>a</sup>	16.62	1.2335	0.43543	-0.065780		
293	16.23	1.4702	0.2265	-0.081369	7	65.5
288	15.74	1.6485	0.1639	-0.088969	7	64.0
283	15.12	1.8894	0.1230	-0.10222	7	82.4
278	14.29	2.2623	0.1082	-0.12780	7	87.5
273	13.30	2.7423	0.0756	-0.16563	7	82.5
268	11.92	3.4611	0.0510	-0.22297	5	50.0
263	10.27	4.3508	0.0547	-0.29871	5	43.6
258	9.00	3.9861	0.0436	-0.17801	4	109.

<sup>a</sup> Reference values from [7].